

Exploration of Melt Spinning as a Route to Large Volume Production of Skutterudite Thermoelectric Materials.

James Salvador



*David Brown and
David Miller*



*Hsin Wang and
Andrew A. Wereszczak*



james.salvador@gm.com





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GM R&D Thermoelectrics Team:

Researchers:

Gregory P. Meisner
Mike Reynolds

Postdocs:

Xun Shi, Jung Cho, Zuxin Ye

Engineering Operations:

Kevin Rober
John Manole

Gov. Contracts:

Ed Gundlach,
Amanda Demitrish
Rick Leach

Management:

Jan Herbst
Mark Verbrugge

GMPT Integration & Testing:

Jennifer Staneck
Joshua Cowgill

Stuart Smith

Collaborators/Subcontractors:

Marlow Industries: Jeff Sharp, Jim Bierschenk, Josh Moczygemba, and **Alan Thompson**

Oak Ridge National Laboratory: Hsin Wang, Andy Wereszczak

University of Nevada, Las Vegas: Changfeng Chen, Yi Zhang

Future Tech: Francis Stabler

Heat Technology, Inc

Emcon (Faurecia)

Shanghai Institute of Ceramics: Lidong Chen

University of Michigan: Ctirad Uher

University of South Florida: George Nolas

Brookhaven National Laboratory: Qiang Li

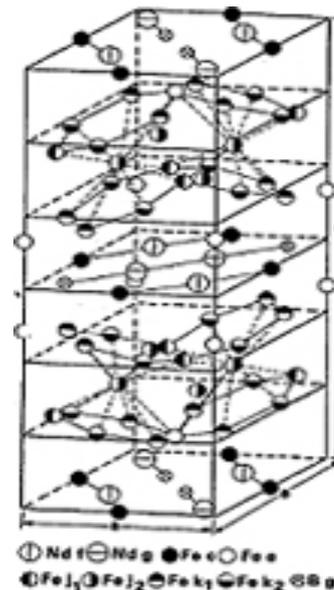
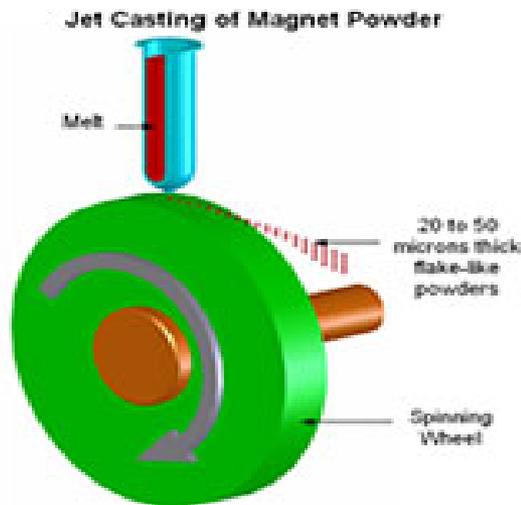
Michigan State University: Don Morelli

General Electric Global Research: Todd Anderson, Peter DeBock



Melt Spinning: Back Ground

- The use of melt spinning in metallurgy dates back to the early 1960's for the production of amorphous metallic materials.
- The technique was developed into a continuous feed process in the mid 1970's
- Over the years the technique has been developed to produce more and more complex intermetallic phases such as the rare earth magnets $\text{Nd}_2\text{Fe}_{14}\text{B}$ (NIB)
- Magnequench was formed from the development of NIB at GM R&D in the mid to late 80's



Melt Spinning and Thermoelectric Materials

➤ Some of the first reports of the application of melt spinning to thermoelectric materials came around 2007

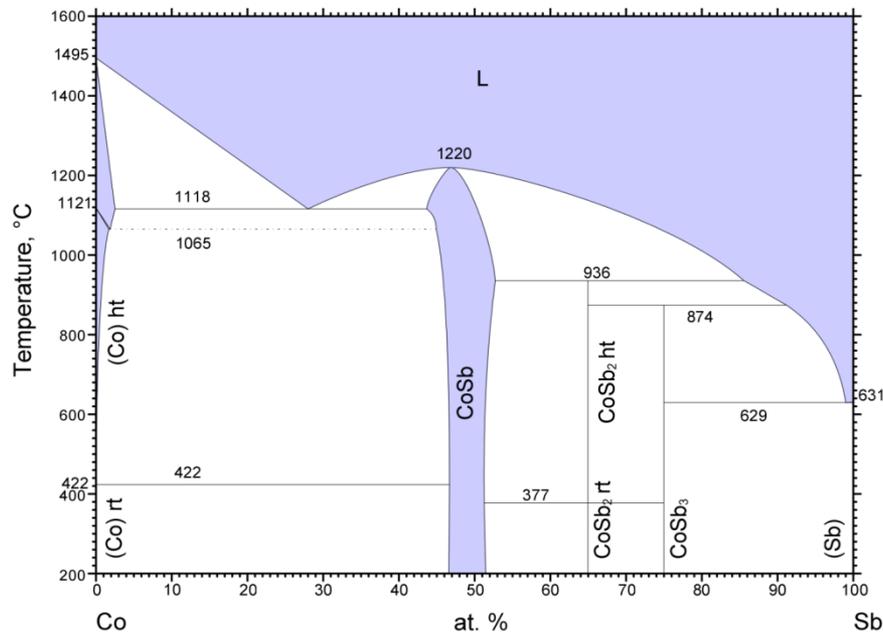
H. Li and X.F. Tang at Wuhan University China reported the MS production of Yb-filled skutterudites. The focus of these efforts was to make nanostructured thermoelectric materials with improved properties.

➤ Subsequently Q. Li at Brookhaven National Lab and T. Tritt from Clemson have reported the use of MS for the production of both n-type (Clemson) and p-type (BNL) skutterudite materials. BNL has advanced to other materials systems such as HMS. Other systems prepared by this method include clathrates and half-Heuslers.

➤ There has been many recent reports on improved thermoelectric properties of MS Bi-Te based materials, and the improvement is attributed to nanostructuring imparted by the MS process.

Skutterudite-Based Thermoelectric Materials

- We concluded from our last program that the traditional method of preparing skutterudite materials was too time consuming and energy intensive to be economically viable.
- This is due to the peritectic decomposition of the CoSb_3 below its melting point: these materials cannot be melted and cast, but require lengthy heat treatment.
- Skutterudite materials can also be made by mechanical alloying



Traditional preparation of n-type filled-skutterudites

Co and Sb shot pre-melted by induction at 1400°C in a ratio of 1:3 in BN. Followed by adding Ba, Yb and Sb to the desired composition and re-melting at 1200°C for 5 min.



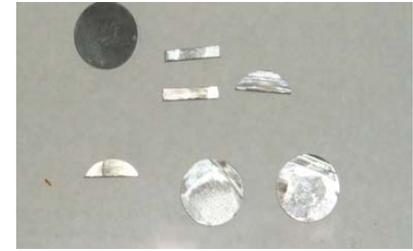
The resulting ingot is not the desired skutterudite phase since skutterudites decompose above 840°C; products are: $\text{CoSb}_2 + \text{Sb} + \text{YbSb}_2$

2 weeks annealing at 750°C



After annealing the product is $\text{Ba}_y\text{Yb}_x\text{Co}_4\text{Sb}_{12}$

Annealed samples are ground into powder for hot pressing or spark plasma sintering

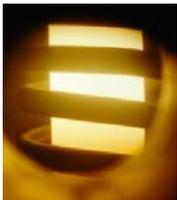


Resulting billets are >98% fully dense pure phase skutterudite

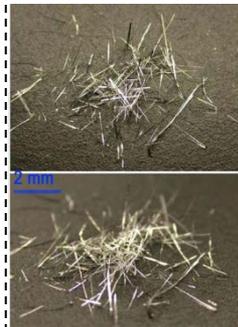
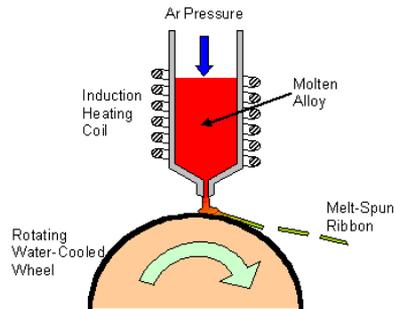
For traditional method 2 weeks preparation time used

Proposed melt-spin preparation of n-type filled-skutterudites

Co and Sb shot pre-melted by induction at 1400°C in a ratio of 1:3 in BN. Followed by adding Ba, Yb and Sb to the desired composition and re-melting at 1200°C for 5 min.

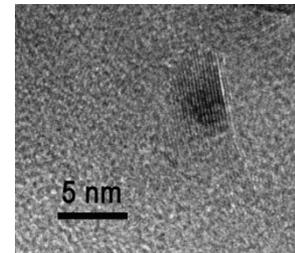


Resulting ingot melt-spun using specified temperature, ejection pressure, and wheel speed



Ribbon product: not the desired skutterudite phase

Fine-grain structure of the rapidly cooled ribbon product facilitates solid-state reaction, eliminating need for lengthy annealing



Ribbons are ground into powder for spark plasma sintering

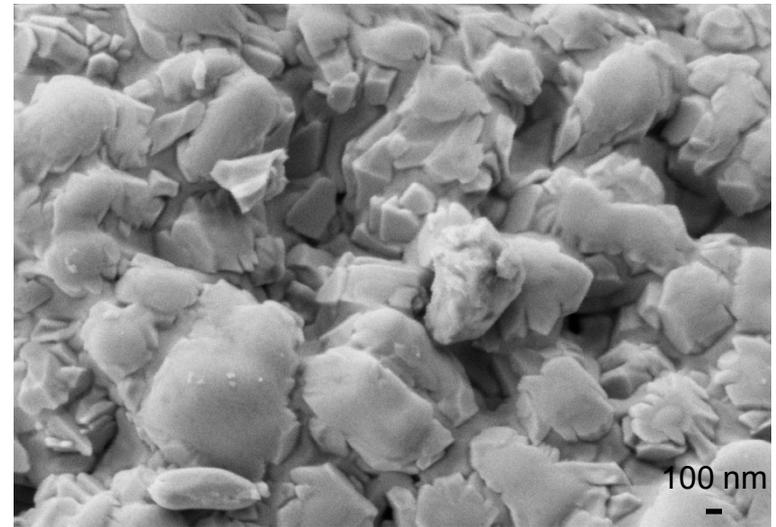
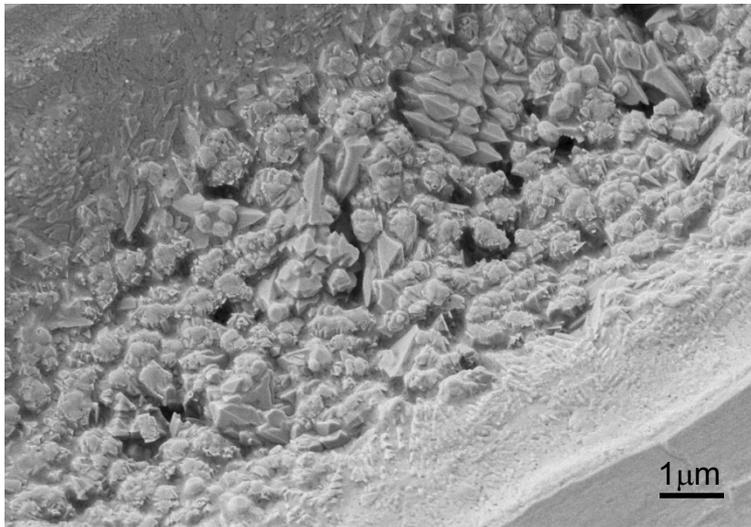
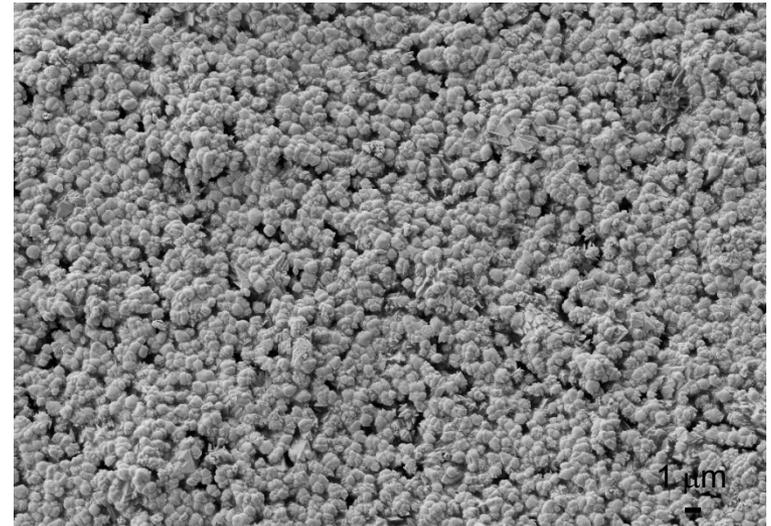
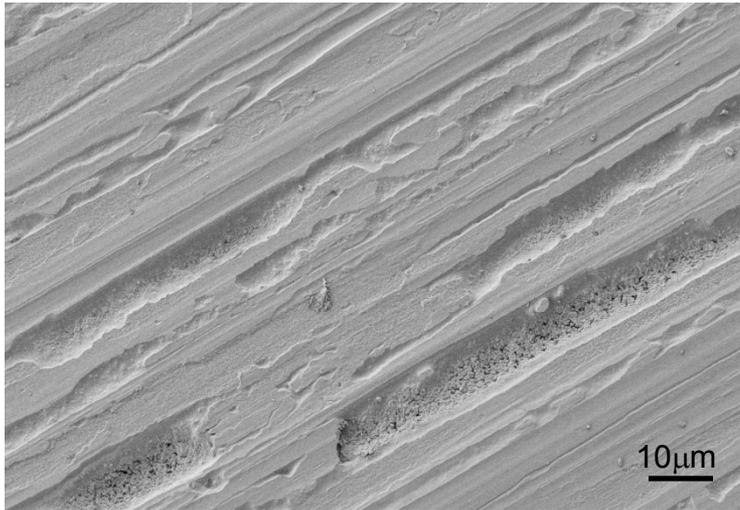


Resulting billets are >98% fully dense pure phase skutterudite

For melt spinning method preparation time is reduced to 4-5 hours



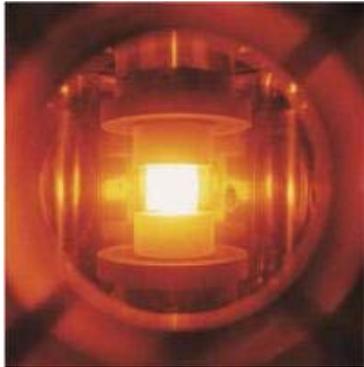
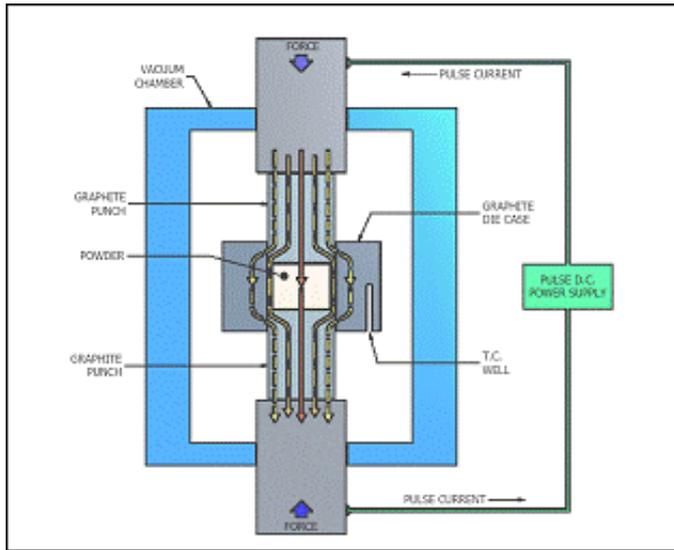
Microstructure of as-spun materials



Contact Surface

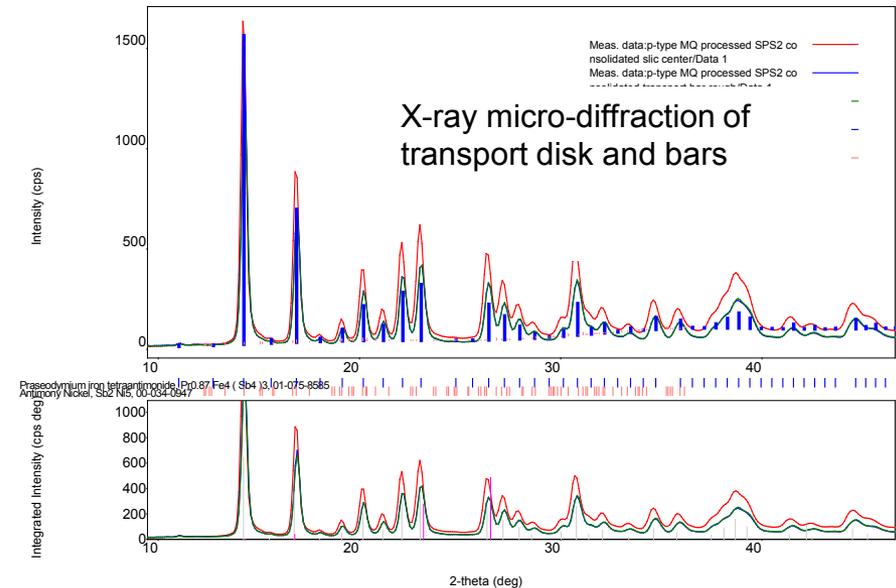
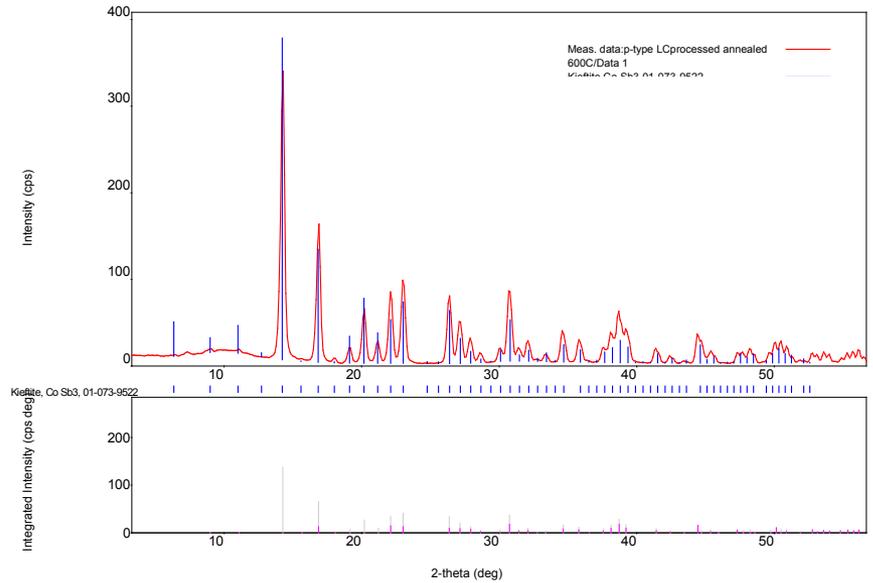
Free Surface

Direct Sintering of As-Spun Ribbons

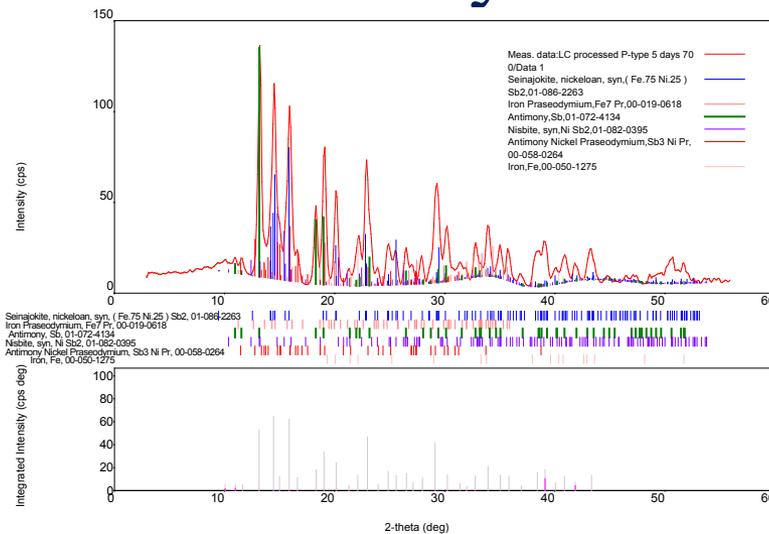
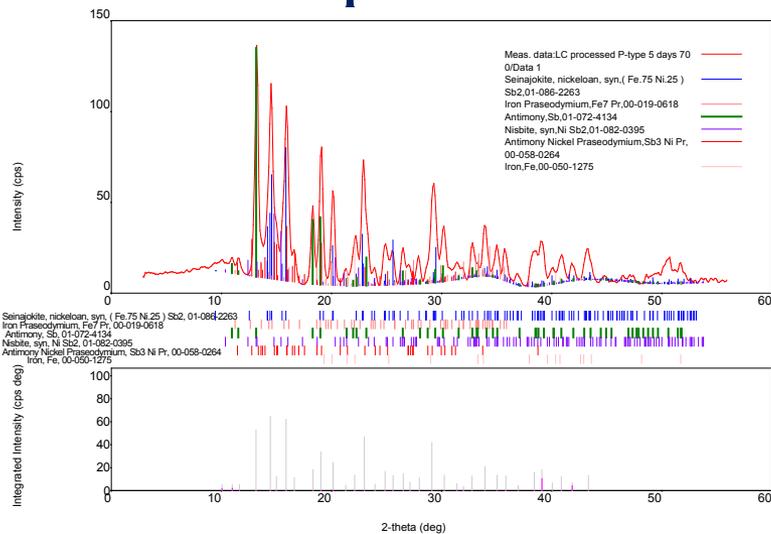


This method is scalable.

We have obtained pure phase billets on the 5 g (1/2" diameter) to the 80+ g scale (3.0 cm diameter/1.5 cm thick).



Direct Conversion to Pure Skutterudite Phase Can be Accomplished in Minutes Instead of Days.



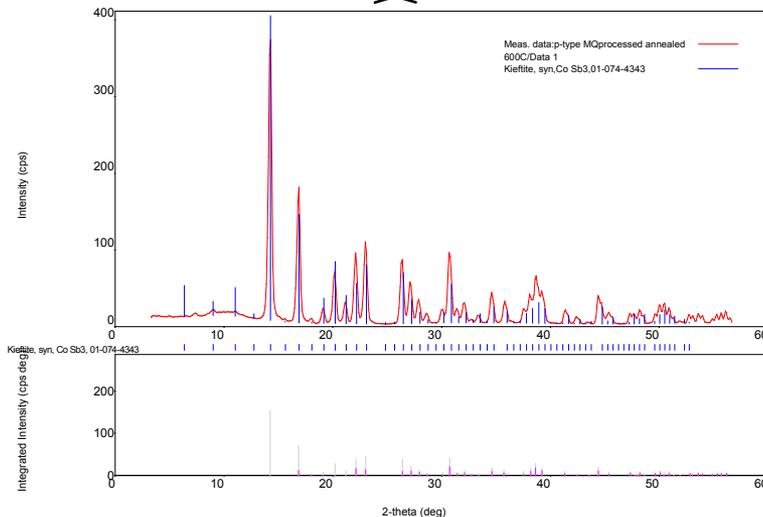
SPS for 20 min.

Annealed for 1 week at 650°C

This was found to be true for both n- and p-type skutterudite materials and did not matter if the materials were rapidly quenched (higher wheel speed) or slow quenched

N-type materials are more stable at higher temperatures

P-type tended to decompose in the SPS if sintering temperature exceeded 600 °C

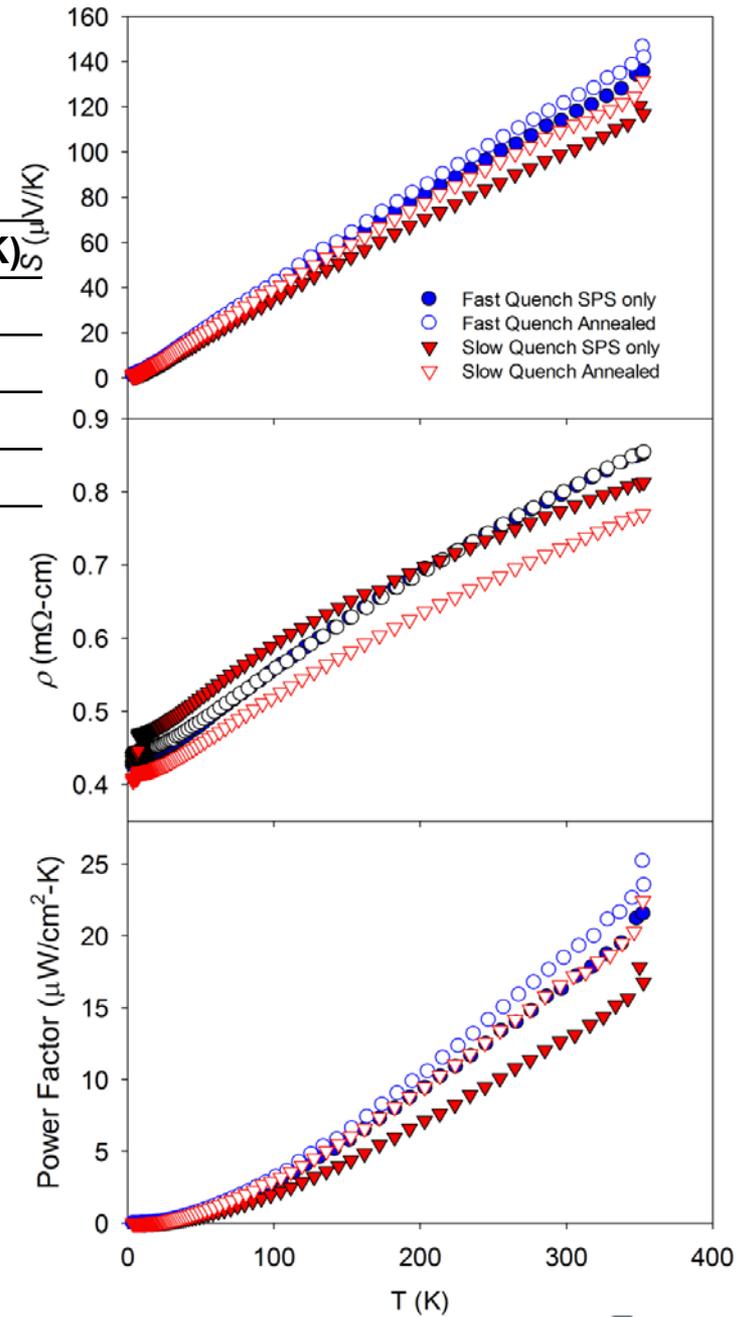
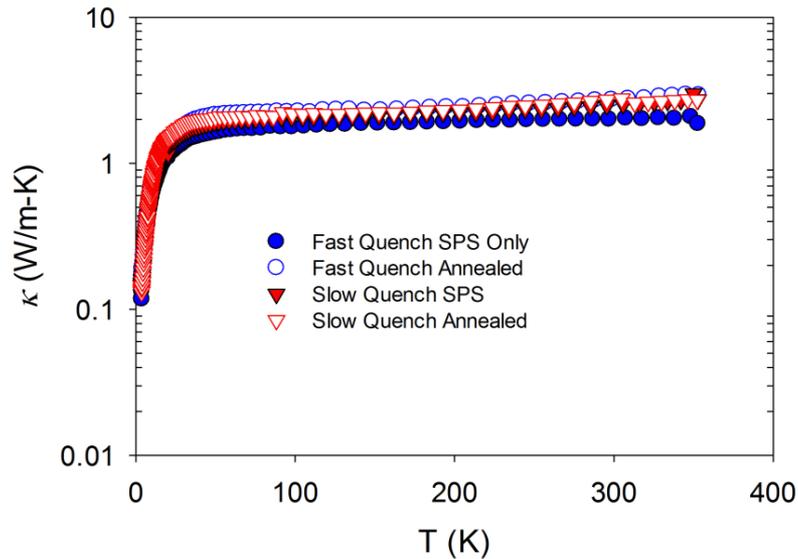


Transport Property Evaluation P-Type Materials

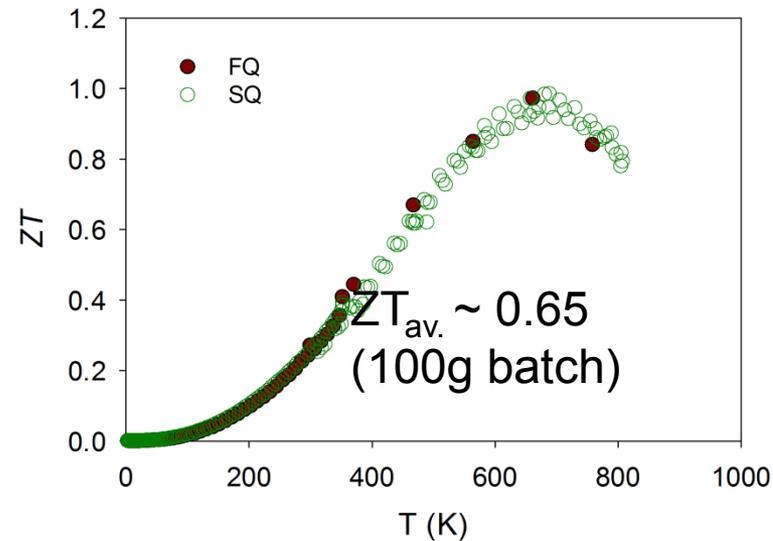
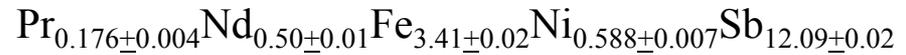
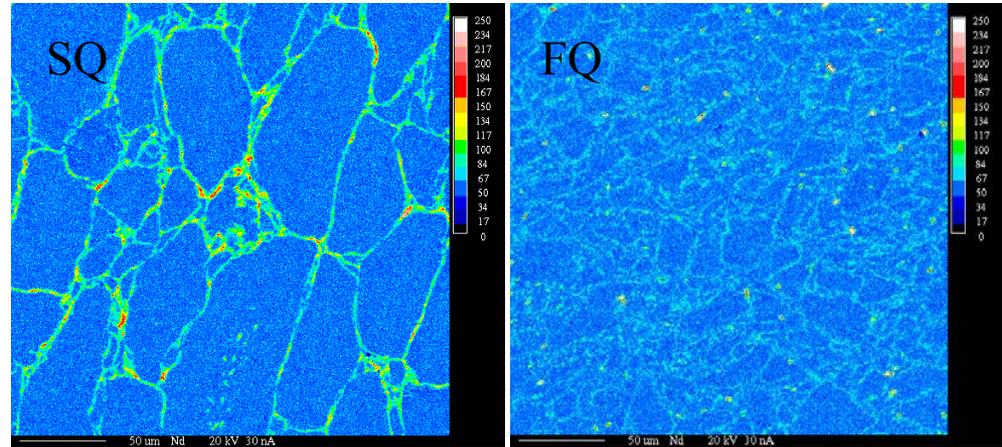
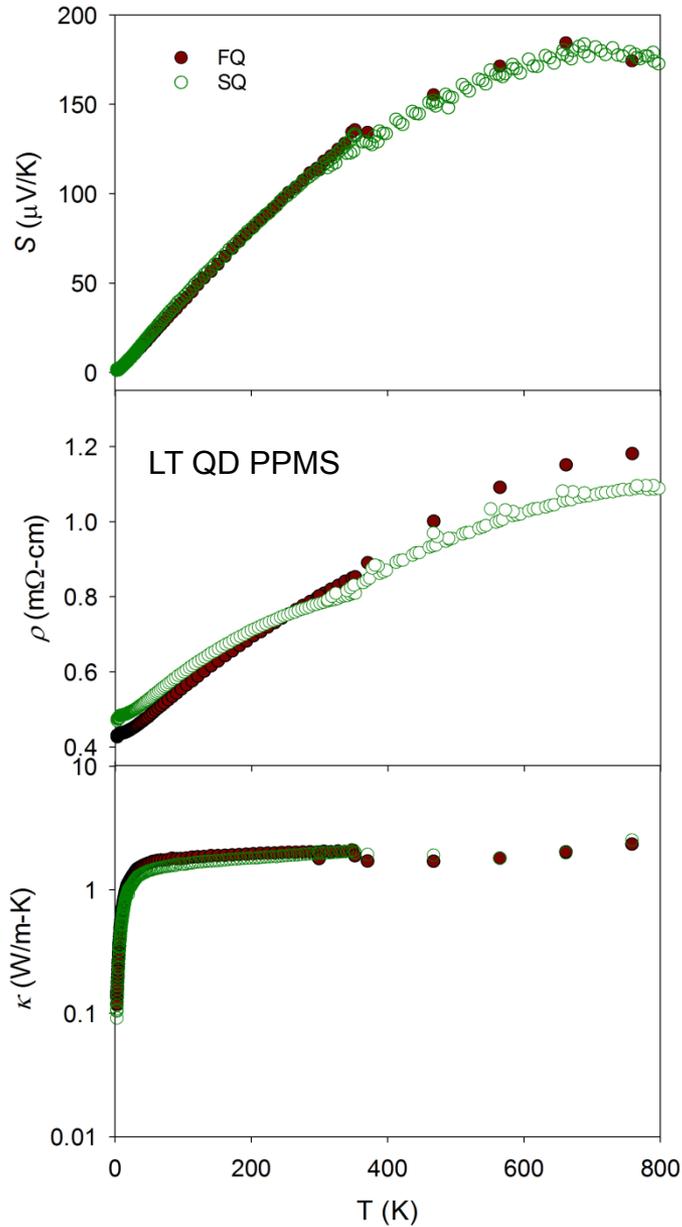
Thermal and electrical transport parameters (300 K)

Sample ID	κ (W/m-K)	S (μ V/K)	ρ (m Ω -cm)	PF (μ W/cm ² -K) S (μ V/K)
FQ-SPS	2.0	115	0.79	16.3
FQ-An-SPS	2.7	121	0.80	18.4
SQ-SPS	2.5	100	0.77	12.6
SQ-An-SPS	2.7	109	0.72	16.5

FQ = Fast Quench
SQ Slow Quench
An-SPS= annealed and then SPS



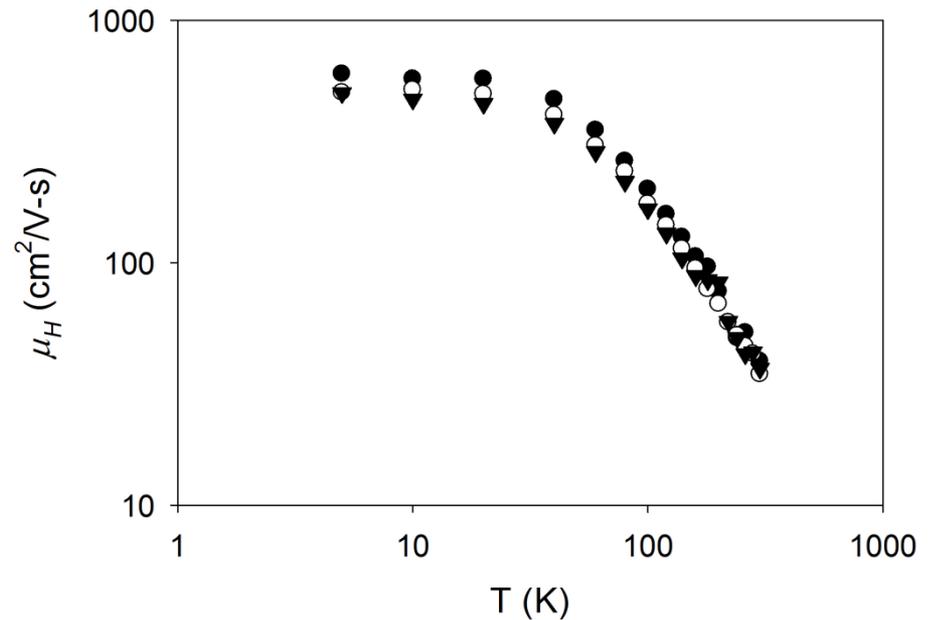
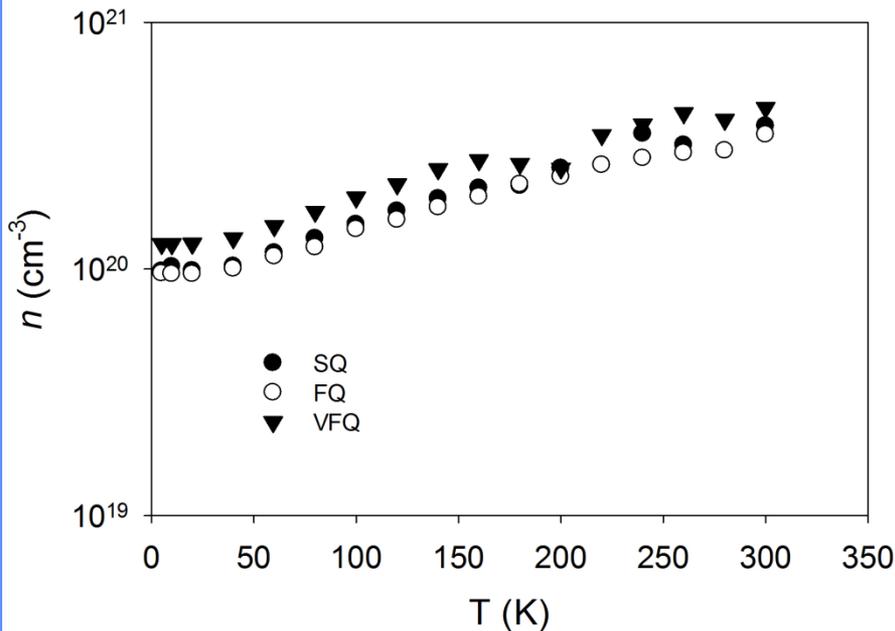
High Temperature Transport Properties and Composition



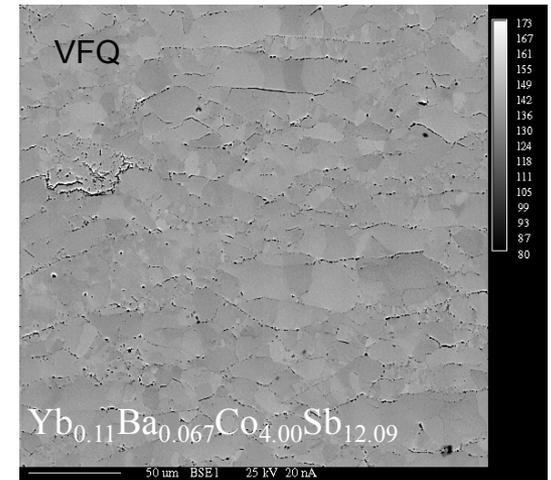
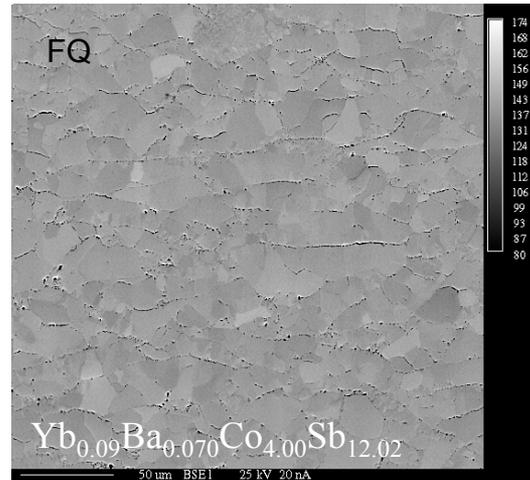
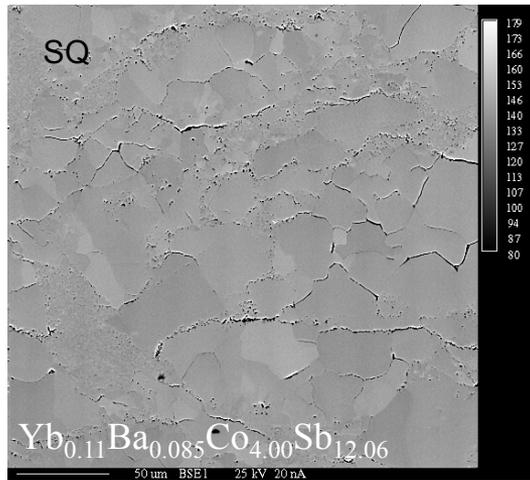
Transport Property Evaluation N-type Materials

Sample ID	κ (W/m-K)	S (μ V/K)	ρ (m Ω -cm)	n (cm ⁻³)	μ_H (cm ² /V-s)	PF (μ W/cm ² -K)
VFQ-SPS	3.5	-114	0.39	4.5×10^{20}	36.6	34
FQ-SPS	3.5	-127	0.46	3.5×10^{20}	34.5	35
SQ-SPS	3.9	-122	0.41	3.8×10^{20}	39.3	35

All samples had the same nominal composition $\text{Yb}_{0.13}\text{Ba}_{0.10}\text{Co}_4\text{Sb}_{12}$

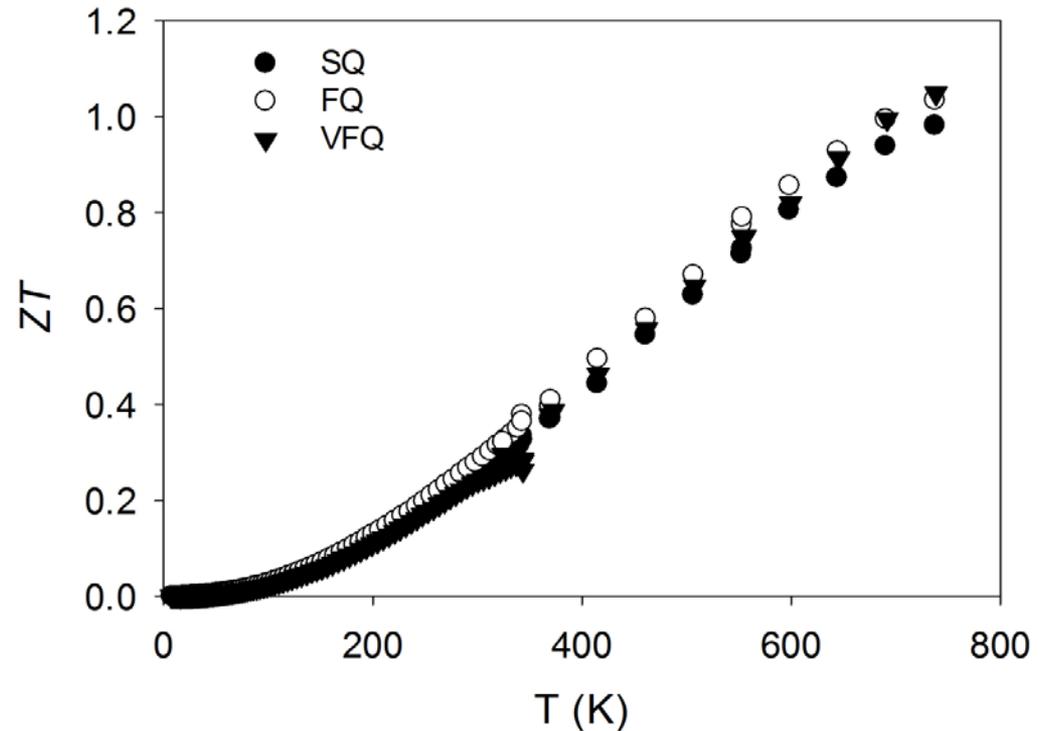
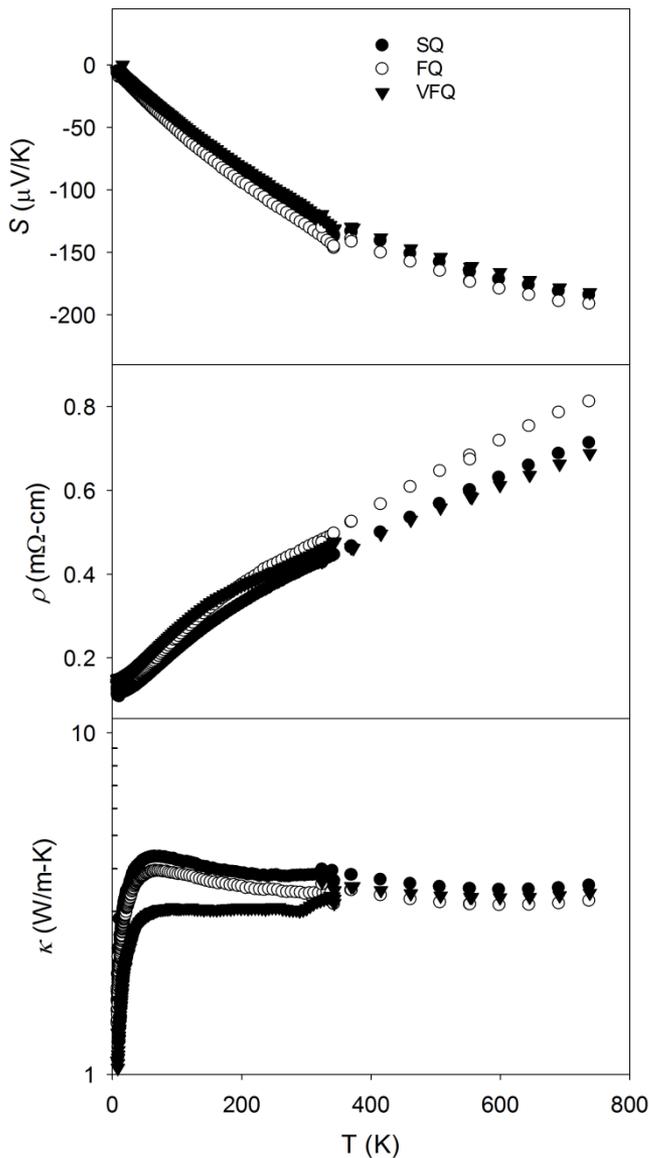


Composition and Microstructure of N-type Materials



- Grain size for VFQ and FQ samples are comparable, and much finer than the SQ samples.
- All samples irrespective of quench rate can be sintered into single phase billets by heat to 650 °C and holding for 10 to 15 min.
- Despite differences in the carrier concentration for the VFQ sample the filling fraction is not significantly higher than the other samples as assessed by EPMA .

Transport Property Evaluation N-type Materials

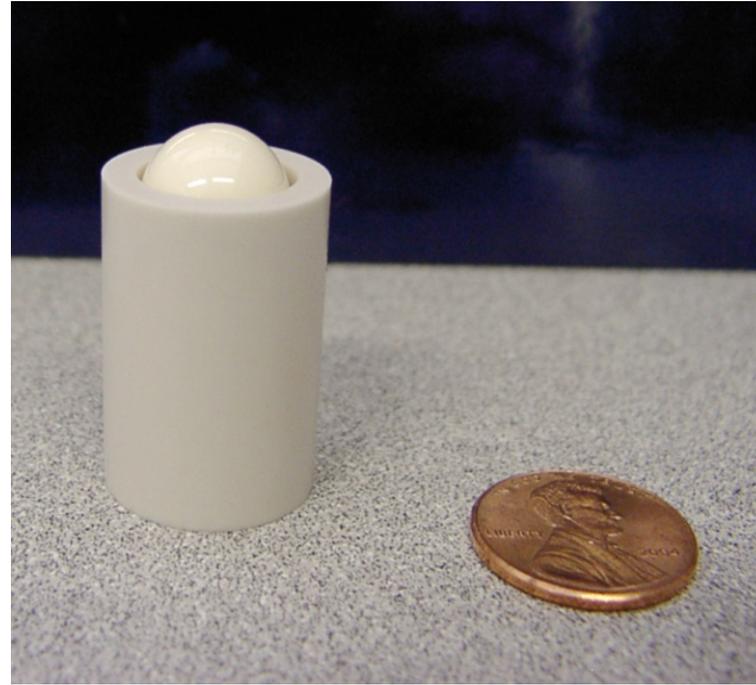


A small and likely statistically insignificant improvement in ZT with a faster quench rate:
($ZT=0.97$ for SQ vs. $ZT=1.05$ for FQ and VFQ at 740 K)

Sample transport properties were repeatable over the heating and cooling cycle.

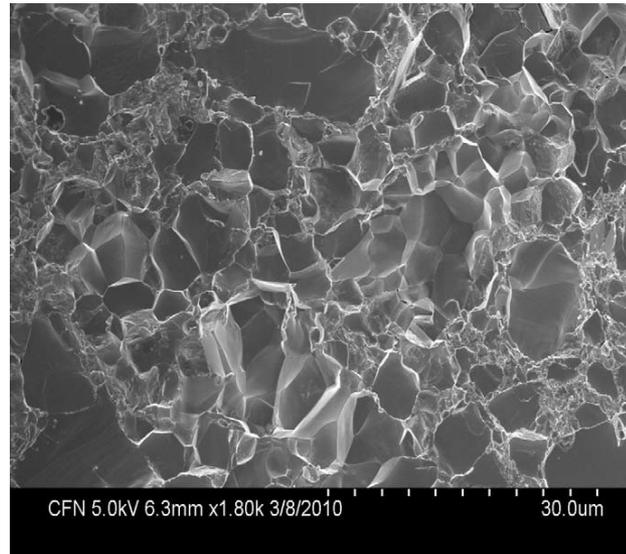
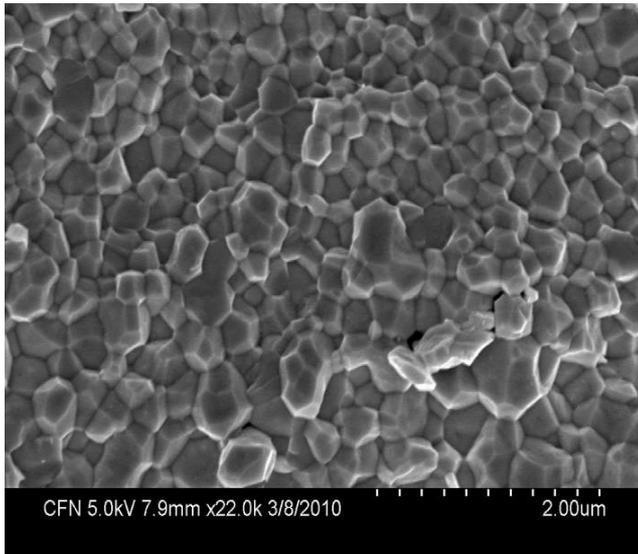
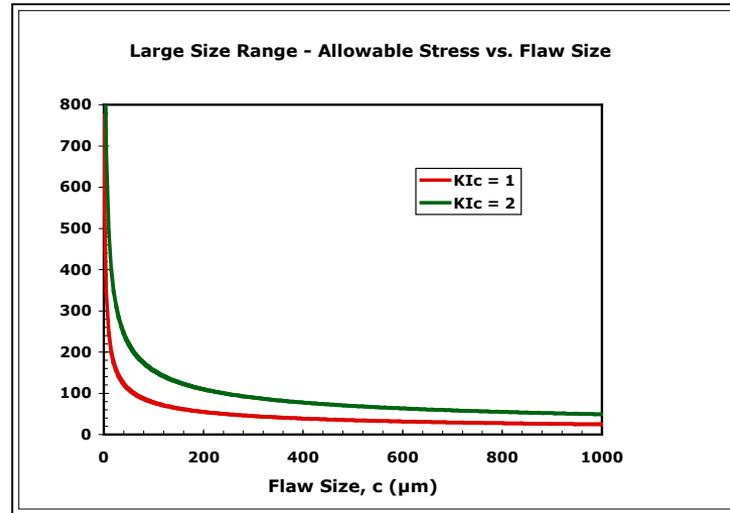
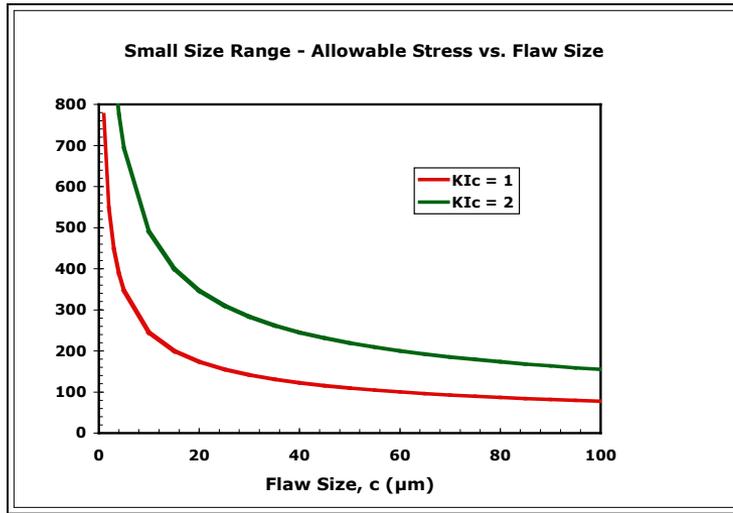
Tests are underway to look at cycling reproducibility.

Mechanical Property Evaluation of Melt-Spun Materials



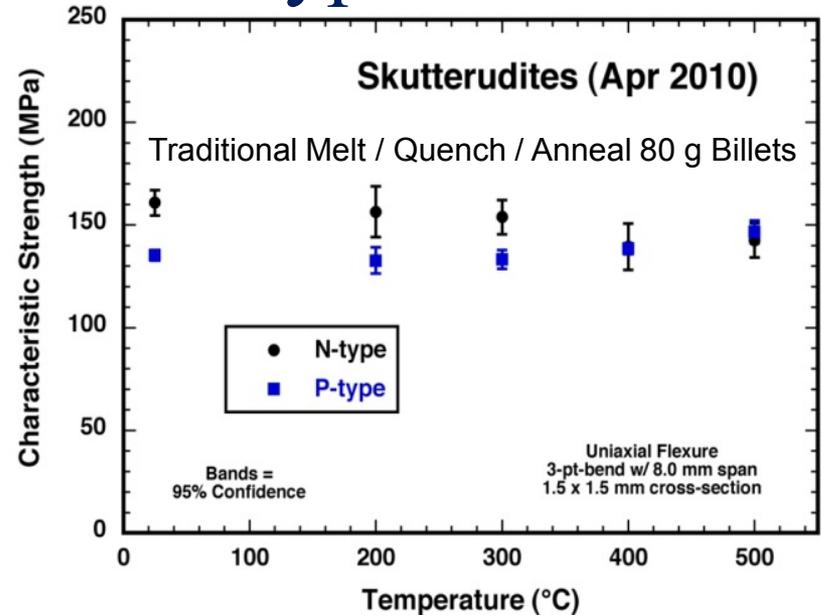
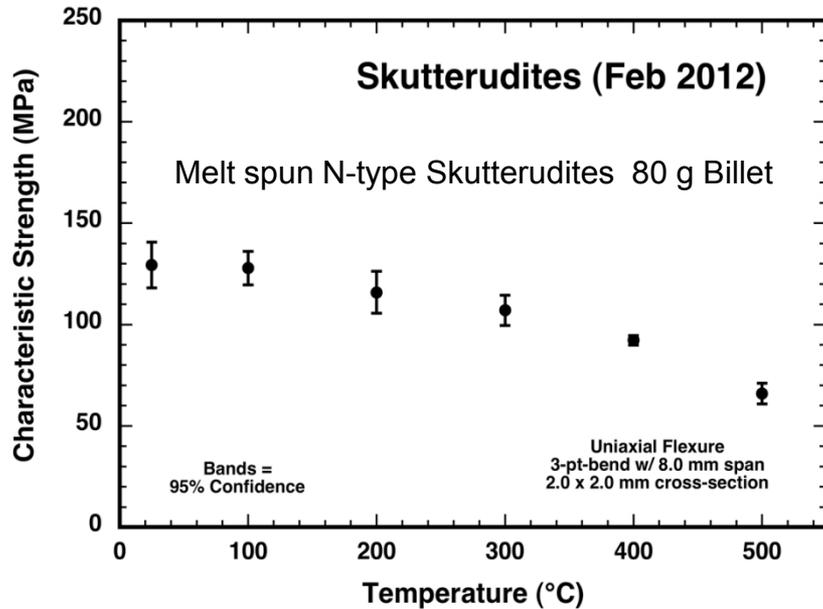
Tensile fracture bars of developmental materials prepared by high volume manufacturing methods were tested to see if their fracture strength is improved compared to materials prepared by the standard melt-quench anneal method.

Does Finer Microstructure Lead To Stronger Materials?



Volume type flaws

Mechanical Property Evaluation N-type Materials



- The data presented here are uncensored. Meaning failure is initiated by surface, edge and volume flaws. The test bars (95 in total) for the melt spun materials were cut into prismatic bars that were 2 x 2 x 10 mm. 20 bars were tested at room temp and 15 bars at subsequent temperatures
- Two distinct surfaces were present one was a matte finish the other a cut surface, both were tested at room temperature and the matte surface was found to be weaker and so subsequent measurements were performed on the matte surface to get a conservative estimate of the fracture strength.

CTE of n- type material ~ 10.0 PPM to 14 .0PPM

Young's Modulus (RUS) = 139 GPa

Poisson's Ratio (RUS) = 0.20

These values are comparable to those of materials prepared in the standard way.



Other Opportunities for Streamlining Production and Improving Properties



- Net-shape sintering of TE legs to reduce materials loss and increase processing through-put.
- Advantage of potentially eliminating edge and surface flaws that can lead to failure.
- Net shape sintering allows for the formation of TE legs with more exotic shapes for high packing densities
- Can eliminate sharp corners for TE legs which FEA shows to be concentrated centers of stress when under large temperature gradients.

Concluding Remarks/ Future Work

- Melt spinning combined with Spark Plasma Sintering provides a potential route to the mass production of Skutterudite based thermoelectric materials. This route seems to obviate the long term annealing processes.
- Consolidation of melt spun ribbons is scalable producing phase pure billets from the 5 g to ~80 g scale. There is no reason to believe that this is the limit to the size of billets that can be made.
- Fracture tests performed on FQ n-type materials find that them to be of comparable characteristic strength to materials made by the conventional method, with a weak temperature dependence.
- Thermoelectric properties of the n-type materials compare well with those published in the literature. Power factors are comparable to other Yb/Ba-filled materials produced using conventional methods. Thermal conductivity is about 25 to 30% higher for the MS/SPS case resulting in ZT's that are ~1 to 1.1 at 740 K.
- The p-type materials, due to the very low thermal conductivity approach a ZT of 1 in the same temperature range. Power factors are comparable to those reported to materials made by traditional methods.
- Future work to include pursuing compositions and processing conditions which lower the thermal conductivity of the n-type skutterudites to levels reported for materials made by the traditional methods.
- Continue to optimize p-type compositions to push the onset of intrinsic conduction to higher temperatures while maintaining the very low thermal conductivity values.
- Measure the elastic properties CTE's and fracture strength of p-type materials and examine scaled-up sintering operations.